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HARDENING IN AlN INDUCED BY POINT DEFECTS

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ABSTRACT

Pressureless-sintered AlN was neutron irradiated and the hardness change was examined by Vickers indentation. The hardness was increased by irradiation. When the samples were annealed at high temperature, the hardness gradually decreased. Length was also found to increase and to change in the same way as the hardness. A considerable density of dislocation loops still remained, even after the hardness completely recovered to the value of the unirradiated sample. Thus, it is concluded that the hardening in AlN is caused by isolated point defects and small clusters of point defects, rather than by dislocation loops.

Hardness was found to increase in proportion to the length change. If the length change is assumed to be proportional to the point defect density, then the curve could be fitted qualitatively to that predicted by models of solution hardening in metals. Furthermore, the curves for three samples irradiated at different temperatures and fluences are identical. There should be different kinds of defect clusters in samples irradiated at different conditions, e.g, the fraction of single point defects is the highest in the sample irradiated at the lowest temperature. Thus, hardening is insensitive to the kind of defects remaining in the sample and is influenced only by those which contribute to length change.

1. INTRODUCTION

Irradiation effects of low Z ceramics have been examined extensively. Low Z materials are candidates for the first wall in fusion reactors. If the first wall is constituted from high Z material and high Z atoms are mixed into the plasma by plasma-wall interaction, the temperature of the plasma would decrease and the efficiency of the fusion reaction might be lowered.

AlN is a typical low Z material; however, there have been few studies concerning irradiation effects in AlN because it is difficult to synthesize and sinter to a bulk material. AlN has a high thermal diffusivity and is potentially suited for the first wall of a fusion reactor, which suffers not only 14MeV neutron radiation but a high heat flux.

During irradiation, many kinds of defects are formed in ceramics. The mechanical properties of the ceramics are changed by the formation of these defects. Among the property changes in materials, hardening is a well known effect appearing after irradiation. Hardening has been reported in some irradiated ceramics[1-5]. In particular, point defects play a predominant role in the hardening of $MgO{\cdot}3Al_2O_3$ single crystal[5]. However, no work has been reported on hardness in irradiated AlN.

In this work, the hardness change of AlN after irradiation is examined. Further, the cause of the hardening is also discussed. Finally, we apply the theory of solution hardening to explain the hardness change in irradiated AlN.

2. EXPERIMENTAL PROCEDURE

Pressureless sintered AlN was obtained by Tokuyama Soda. The AlN contains <1% of CaO as a sintering aid. The material was cut into samples 2x4x25mm in size and the largest surface was mechanically polished with diamond paste.

Then the samples were irradiated with neutrons in the Japan Materials Testing Reactor. Estimated neutron fluences(E>1MeV) and temperatures are as follows(Table 1).

Hardness tests were performed with a Vickers hardness tester. The indentation load was 5kg and the indenter was loaded for 15 seconds on the polished surface. The hardness(H_V) was calculated from the following standard formula;

$$H_v = 1.854 \frac{P}{(2a)^2} \quad (1)$$

where P is the indentation load and 2a is the diagonal of the indentation.

The length of the sample was measured with a point-type micrometer attached firmly with a sample holder. The holder allowed reproducibe alignment of the sample and the reading error of the length was within 1μm.

Annealing was conducted at temperatures up to 1400°C. From 100°C to 1000°C, an infrared heating furnace was used for annealing because of its high controllability at relatively low temperatures. Samples were annealed for an hour in a vacuum of 1Pa. Then the furnace was switched to a tungsten heater for the temperature range of 1100 to 1400°C. Samples were annealed also for an hour while the inside of the furnace was kept at a vacuum of 10^{-4}Pa. After annealing at a certain temperature, the samples were taken out to the ambient atmosphere and cooled down to room temperature. The hardness and length of the samples were measured. Then the samples were annealed at a higher temperature. This annealing-measurement cycle was conducted repeatedly.

3. RESULTS AND DISCUSSION

3.1 Hardening by Point Defects

Figure 1 shows values of hardness as a function of annealing temperature in AlN irradiated at the three different temperature. The hardness of all three samples is seen to increase by 37 to 51% after irradiation compared to the hardness of the unirradiated sample[6]. For the samples irradiated at 470 and 785°C, the hardness stays almost constant up to annealing temperatures of 800 and 900°C, respectively. After annealing above these temperatures, the hardness decreases gradually and finally reaches a value ~1100kg/mm^2, which is close to the hardness of the unirradiated sample, 950kg/mm^2. On the other hand, the hardness begins to decrease rapidly after 100°C annealing in the sample irradiated at 100°C. The temperatures at which hardness starts to decrease vary with the irradiation condition. As the irradiation temperature goes up, the transition temperature increases. It is interesting that the transition temperatures of the sample irradiated at 100 and 785°C are almost the same as the irradiation temperatures.

Figure 2 shows plots of length change against annealing temperature in irradiated AlN. The behavior is very similar to that of the hardness although the transition temperatures are clearer than those of the hardness curves. The important point is that the transition temperatures of both the hardness and length change are almost the same for each irradiation temperature. This implies that both hardness and length change are controlled by the same defects.

Yano et al. suggested that the predominant process occurring during annealing is vacancy-interstitial recombination[7]. Swelling is caused by the formation of point defects and, to a first approximation, the length change is one third of the volume change. Thus, the length change after annealing reflects the decrease in the numbers of vacancies and interstitials by the same amount for each. Similarly, the decrease in hardness after annealing can be explained by the decrease in the number of these point defects.

When the hardness is plotted against length change during annealing, the results are as shown in Fig. 3. All the data of hardness vs. length change align on a single curve. This means that the hardening is independent of the irradiation condition and only depends on the length change, which in turn reflects the number of defects present.

Table 1 Irradiation condition

Fluence(nm^2)	$8.3x10^{22}$	$2.4x10^{24}$	$5.2x10^{24}$
Irradiation Temperature (°C)	100	470	785

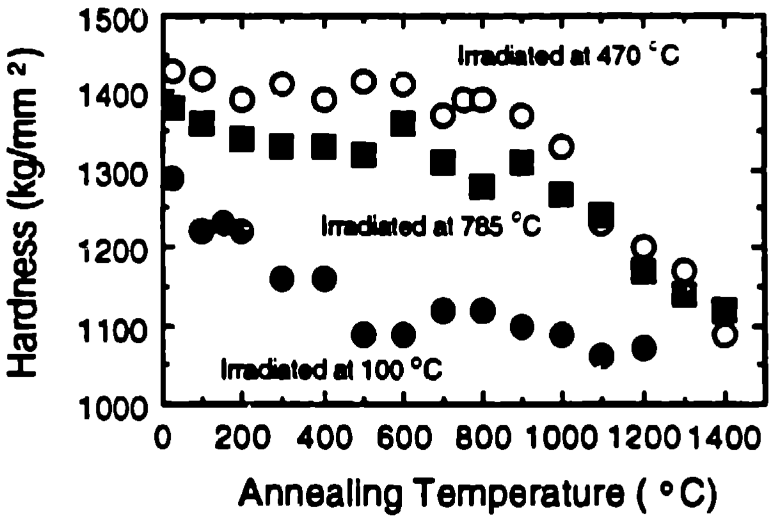

Fig.1 Hardness change in irradiated AlN after annealing.

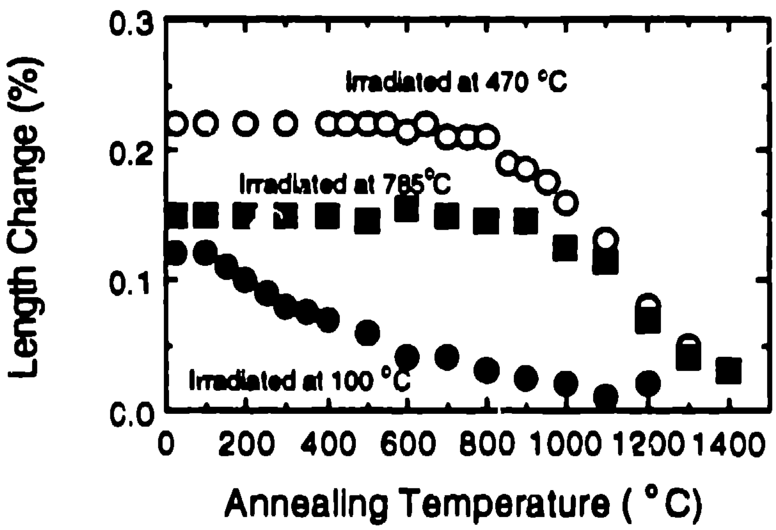

Fig.2 Length change in irradiated AlN after annealing.

Let us consider the relation between the number of defects and the hardness change. For simplicity, assume that only primary vacancies and interstitials remain in the irradiated AlN. Each interstitial or vacancy expands or contracts the crystal in its vicinity. The resulting strain field can interact with that of a dislocation, leading to pinning. Similarly, when an impurity atom is placed substitutionally or interstitially into the crystal, the strain field is qualitatively the same as that of intrinsic point defect. Thus, the mechanism of the hardening in an irradiated AlN is similar to that of solution hardening.

The yield stress change due to solution hardening from asymmetric point defects is

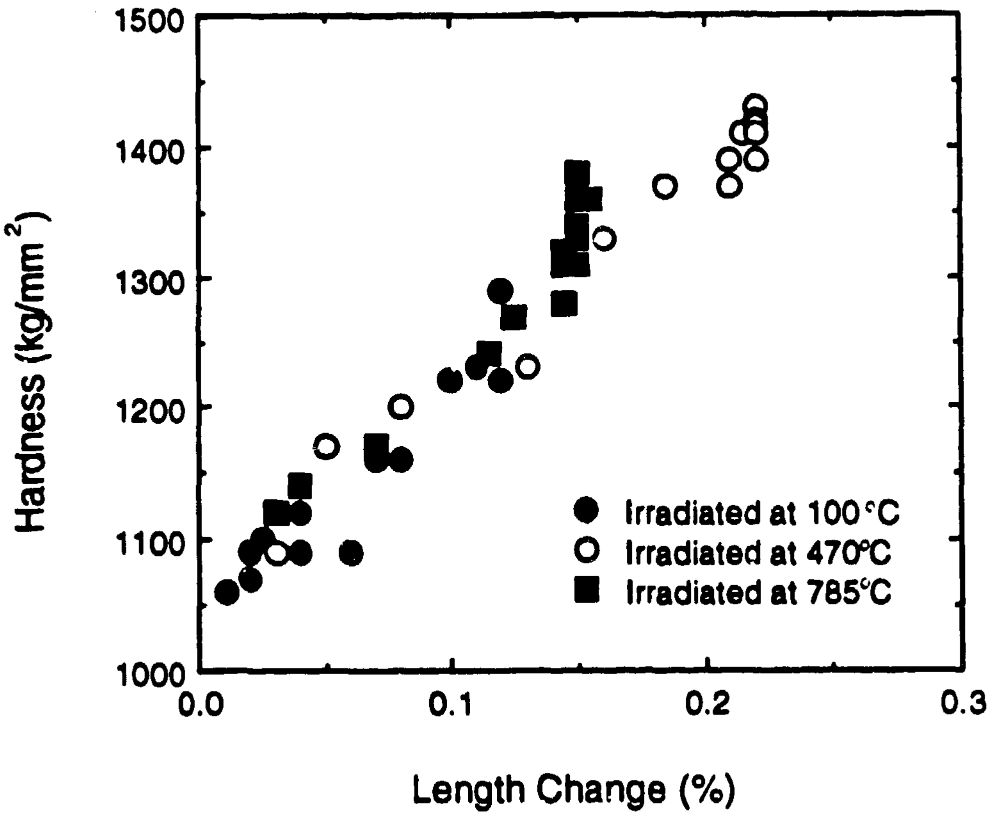

Fig.3 The Hardness plotted against the length change.

$$\tau_h=\tau_0+\frac{1}{3}\mu\Delta\varepsilon c_i^{1/2} \tag{2}$$

where τ_h is the yield stress of the hardened material, τ_0 is the yield stress of the control sample, μ is shear modulus, $\Delta\varepsilon$ is transverse strain of the tetragonal distortion and c_i is the concentration of solute atoms. This equation shows that the yield stress change should be proportional to the square root of the concentration of solute atoms. Following equation (2), we propose that the hardness increase after neutron irradiation should be given by:

$$H_i=H_0+Ac_d^{1/2} \tag{3}$$

where H_0 is the hardness of the unirradiated sample(950kg/mm^2), H_i is the hardness after irradiation, c_d is the concentration of point defects and A is a constant. The validity of equation (3) is demonstrated in Fig.4, where H_i-H_0 are plotted logarithmically against the length change; proportional to one third of c_d. Most of the points lie on a straight line. Furthermore, the slope of the straight line is 0.53, i. e., almost equal to 1/2. This fact shows the validity of the principle that irradiation hardening can be explained as solution hardening by equation (3).

Although the relation between the hardness change and the number of defects is quite clear, the exact number of the defects and their interaction with dislocations is uncertain. Interstitials should have the largest strain field with both a dilatational and shear component to interact with dislocations. However, it is also possible that the important defects are small clusters, as discussed in the next section.

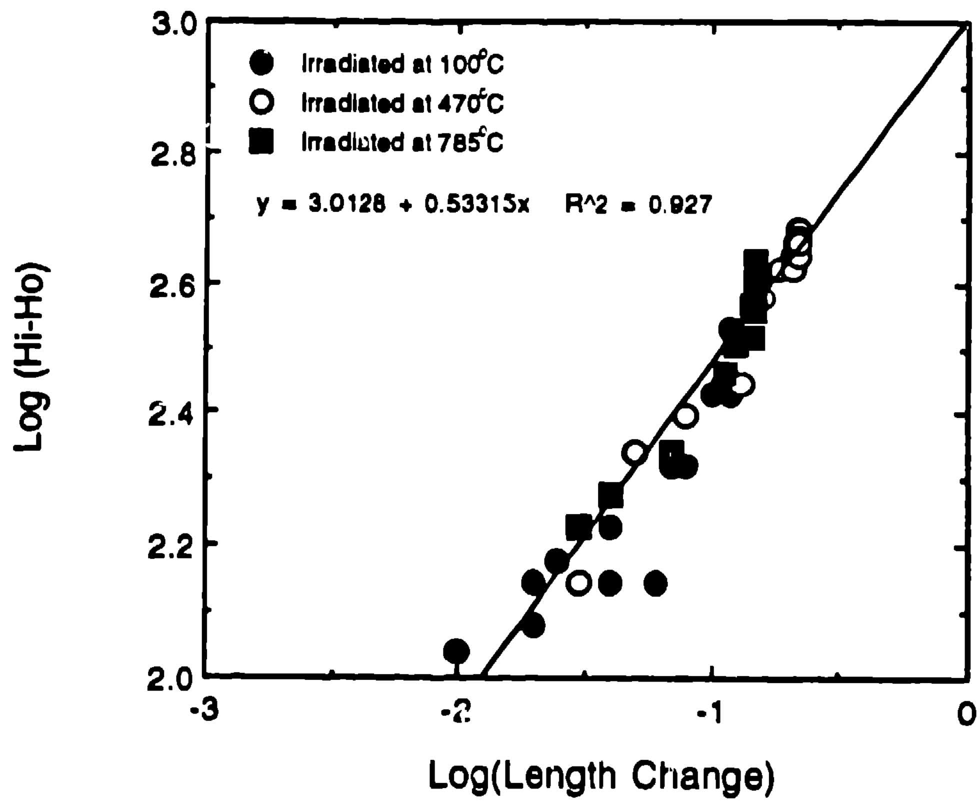

Fig.4 H_i-H_0 plotted logarithmically against the length change

3.2 Effect of Small Defect Clusters

In the former section, we assume that defects remaining in the sample are only primary point defects except dislocation loops and ignore the possible existence of defect clusters. In fact, small vacancy or interstitial clusters should exist in the sample[6]. Fig. 2 shows that the length change decreases almost linearly beyond the transition temperature. Similar behavior has been reported in many ceramics[6,10-12]. The activation energy for the recombination of an interstitial and a vacancy should have a single definite value. If only the primary interstitial-vacancy recombination occurs during annealing, the number of defects should not decrease linearly with annealing temperature, as the length change does in Fig.2. This means that the activation energy for the annihilation of defects must have more than one value. Further, the temperatures at which the length begins to decrease are different for the various irradiation temperatures. This dependence on irradiation temperature cannot be explained by the primary point defect model.

The most probable case is the existence of small defect clusters. As described in the next section, small dislocation loops are observed in some samples. Thus, it is natural to think that defect clusters not large enough to form visible loops exist in the sample. The size distribution of the clusters would be different if the irradiation temperature and fluence change. If there are small defect clusters in the irradiated sample, the volume change is no longer directly proportional to the number of point defects. When a small cluster is formed by combining several interstitials or vacancies, relaxation of volume will occur and the volume change will be smaller. However, Fig. 3 indicates that hardening depends only on the length change and not on the irradiation condition. Thus, the hardening is controlled by how the clusters expand the crystal and pin down dislocation movement.

3.3 Effect of Dislocation Loop

The observation of dislocation loops in irradiated AlN has been described previously[6,7,13]. No loops could be detected in the sample irradiated at 100°C. However, this sample shows hardening and a decrease in hardness after annealing. Thus, hardening by point defects is confirmed. On the other hand, dislocation loops are observed in the sample irradiated at 470 and 785°C. The loops remain even after annealing at 1400°C for 1hour. After annealing, the hardness is still higher than the unirradiated state by about 10%. Since the length change is also still positive, it is not likely that the remaining hardness increment is the contribution of dislocation loops. In the case of irradiated spinel and SiC, there is no contribution of loops to the hardening[5,6]. AlN begins to decompose at 1500°C in vacuum and so it is difficult to measure the length change above 1500°C. However, it is concluded that point defect clusters remain in small numbers even after 1400°C annealing and is the cause of the small hardening in the sample. Thus, dislocation loops are thought to play little role in the hardening in irradiated AlN.

4. CONCLUSION

1) Hardening and length change were observed in AlN neutron irradiated at various temperatures.
2) Both hardness and sample length decrease proportionately during recovery by annealing.
3) If we assume that the length change is due to remaining primary point defects, the data show that hardening is proportional to the square root of the concentration of point defects and is therefore a case of solution hardening.
4) Hardening may be due to small defect clusters rather than point defects but dislocation loops produced by high temperature annealing are not important in hardening.

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